

PTO 08-6932

CC=JP DATE=19870714 KIND=A
PN=62158737

STABILIZED POLYOLEFIN COMPOSITION
[Anteikasareta Poriorefin Soseibutsu]

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UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. August 2008

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(19): JP
DOCUMENT NUMBER	(11): 62158737
DOCUMENT KIND	(12): A
	(13): PUBLISHED UNEXAMINED APPLICATION (Kokai)
PUBLICATION DATE	(43): 19870714
PUBLICATION DATE	(45):
APPLICATION NUMBER	(21): 61001173
APPLICATION DATE	(22): 19860107
INTERNATIONAL CLASSIFICATION	(51): C08L 23/02; C08K 5/00
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APPLICANT	(71): CHISSO CORPORATION
TITLE	(54): STABILIZED POLYOLEFIN COMPOSITION
FOREIGN TITLE	[54A]: ANTEIKASARETA PORIOREFIN SOSEIBUTSU

1. Title

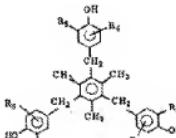
Stabilized Polyolefin Composition

2. Claims

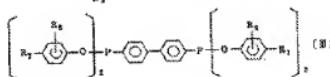
(1) A stabilized polyolefin composition that is prepared by compounding, in 100 parts by weight of a polyolefin, from 0.01 to 1 part by weight each of a 6-hydroxychroman compound represented by general formula I below (hereinafter referred to as compound A) and a phenolic compound represented by general formula II below (hereinafter referred to as compound B) or a phosphonite compound represented by general formula III below (hereinafter referred to as compound C):



(1)



(2)



(wherein R₁, R₂, and R₃ discretely represent hydrogen atoms or the same kind or different kinds of alkyl groups having from 1 to 4 carbon atoms; R₄ represents an alkyl group or alkylene group having from 1 to 16 carbon atoms; and R₅, R₆, R₇, and R₈ discretely represent hydrogen

* Numbers in the margin indicate pagination in the foreign text.

atoms or the same kind or different kinds of alkyl groups having from 1 to 8 carbon atoms).

(2) The stabilized polyolefin composition stated in Claim 1, wherein, in general formulas I, II, and III, the alkyl groups represented by R_1 , R_2 , and R_3 are methyl groups; the alkyl group represented by R_4 is a hexadecyl group; and the alkyl groups represented by R_5 , R_6 , R_7 , and R_8 are t-butyl groups. /2

(3) The stabilized polyolefin stated in Claim 1, wherein tocopherol is used as compound A.

(4) The stabilized polyolefin stated in Claim 1, wherein 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene is used as compound B.

(5) The stabilized polyolefin stated in Claim 1, wherein tetrakis(2,4-di-t-butylphenyl)-4,4'-biphenylene-di-phosphonite is used as compound C.

3. Detailed Description of the Invention

[Field of Industrial Application]

The present invention pertains to stabilized polyolefin compositions. More specifically, it pertains to nontoxic polyolefin compositions that exhibit excellent resistance to oxidation degradation of polyolefin in a melting and kneading process.

[Related Art]

Polyolefins are generally molded at a temperature that is higher than the melting points of said polyolefins, but, in this process,

they undergo oxidation degradation due to the heat for melting and kneading, and the molecular chains of said polyolefins are severed or cross-linked. As a result, various problems occur. That is, the decrease of the molecular weight caused by the severing of the molecular chains leads to decreased mechanical strength, while the crosslinking leads to decreased processability, and the oxidation degradation brings about the problem of coloration and odor.

Furthermore, because polyolefins--especially polypropylene polymers--have tertiary carbon atoms, which are susceptible to oxidation in said polymers, they have a problem in their resistance to thermal oxidation degradation in a melting and kneading process (hereinafter referred to as thermal process stability). Accordingly, heretofore, phenolic antioxidants having a low molecular weight, such as 2,6-di-t-butyl-p-cresol (BHT) and the like, have been widely used for the purpose of preventing the thermal oxidation degradation of polyolefins in a melting and kneading process, that is to say, as the process stabilizer.

However, the molded products that are molded from compositions in which BHT is compounded have a problem of discoloration, especially when they are placed in an alkaline environment. For this reason, the use of vitamin E (tocopherols) as the process stabilizer is known, but, in the case of using tocopherols alone, desired thermal process stability cannot be achieved unless tocopherols are used in a large quantity. When they are used in a large quantity, however, there

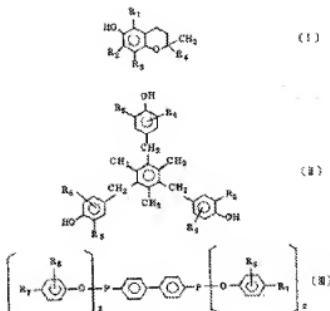
arises the problem of considerable coloration. In order to solve these problems, it is known to use tocopherols concomitantly with phosphoric acids (JP-A-S51-62843); with metal salts of glutamic acid or aluminum complex salts, typical examples of which are hydrotalcites (JP-B-S60-16456); with one or more kinds selected from alkylbenzene-based, amine-based, pantothenic acid-based, and coumarin-based compounds (JP-B-S60-16975); with one or more kinds selected from phosphoric acids, oxyacids, and tetrakis[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate]methane and 2,6-di-t-butyl-p-cresol (JP-B-S60-17217); with glycerophosphates (JP-A-S53-133249); with fatty acid partial esters of polyols (JP-A-S53-137244); with one or more kinds selected from saccharides, polyhydric alcohols, and alkali metal compounds of saccharides (JP-A-S53-141354); with thiodipropionic acid esters (JP-A-S54-34352); with polycyclic phenolic compounds (JP-A-S53-114852); or with phosphite compounds (JP-A-S54-55043).

[Problems that the Invention Intends to Solve]

However, the polyolefin compositions that are prepared by the concomitant use of tocopherols with various kinds of compounds that are proposed in the aforesaid JP-A-S51-62843, JP-B-S60-16456, JP-B-S60-16975, JP-B-S60-17217, JP-A-S53-133249, JP-A-S53-137244, JP-A-S53-141354, and JP-A-S54-34352 exhibit to a certain degree the effect of preventing the coloration of said compositions, but not to a satisfactory level, and their thermal process stability is also not

satisfactory yet. The compositions obtained by the concomitant use of tocopherols and polycyclic phenolic compounds, which is proposed in JP-A-S53-114852, have considerably improved thermal process stability, but their coloration inhibiting effect is not quite satisfactory. With respect to the compositions obtained by the concomitant use of tocopherols and phosphite compounds, which is proposed in JP-A-S54-55043, the thermal process stability and coloration inhibiting property are improved substantially but are not quite satisfactory.

The present inventor conducted extensive research to solve the aforesaid problems associated with the aforesaid polyolefins obtained by compounding tocopherols. As a result, it was learned that a composition that is prepared by compounding, in a polyolefin, a 6-hydroxychroman compound represented by general formula I below (hereinafter referred to as compound A) and a phenolic compound represented by general formula II below (hereinafter referred to as compound B) or a phosphonite compound represented by general formula III below (hereinafter referred to as compound C) can solve the aforesaid problems of polyolefins. Based on this finding, the present invention was achieved.



(wherein R₁, R₂, and R₃ discretely represent hydrogen atoms or the same kind or different kinds of alkyl groups having from 1 to 4 carbon atoms; R₄ represents an alkyl group or alkylene group having from 1 to 16 carbon atoms; and R₅, R₆, R₇, and R₈ discretely represent hydrogen atoms or the same kind or different kinds of alkyl groups having from 1 to 8 carbon atoms.)

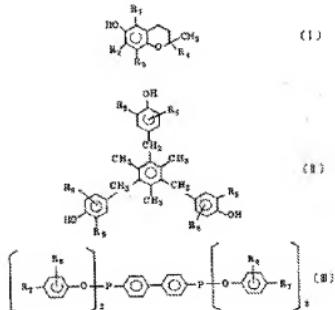
As is evident from the above, the objective of the present invention is to provide a polyolefin composition that exhibits excellent effects on improving thermal process stability and preventing coloration caused by the antioxidants used therein.

[Means for Solving the Problems]

The present invention has the following configuration.

A stabilized polyolefin composition that is prepared by compounding, in 100 parts by weight of a polyolefin, from 0.01 to 1 part by weight each of a 6-hydroxychroman compound represented by general formula I below (hereinafter referred to as compound A) and a

phenolic compound represented by general formula II below (hereinafter referred to as compound B) or a phosphonite compound represented by general formula III below (hereinafter referred to as compound C):



(wherein R₁, R₂, and R₃ discretely represent hydrogen atoms or the same kind or different kinds of alkyl groups having from 1 to 4 carbon atoms; R₄ represents an alkyl group or alkylene group having from 1 to 16 carbon atoms; and R₅, R₆, R₇, and R₈ discretely represent hydrogen atoms or the same kind or different kinds of alkyl groups having from 1 to 8 carbon atoms).

Examples of the polyolefin used in the present invention include: homopolymers of such α -olefins as ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, and the like; random copolymers or block copolymers that are comprised of 2 [a part of the original is missing] of these α -olefins; copolymers of these α -olefins and vinyl acetate, acrylic acid esters, and the like or saponified products of these copolymers; copolymers of these α -olefins and unsaturated

carboxylic acids or anhydrides thereof or reaction products of said copolymers and metal ion compounds; and so forth. Furthermore, the present invention may use modified polyolefins obtained by graft-polymerizing unsaturated carboxylic acids or derivatives thereof to polyolefins or may use mixtures of said modified polyolefins and unmodified polyolefins. Further, the present invention may use mixtures of the aforesaid polyolefins with various kinds of synthetic rubbers (for example, ethylene-propylene copolymer rubber, ethylene-propylene-nonconjugated diene copolymer rubber, polybutadiene, polyisoprene, chlorinated polyethylene, chlorinated polypropylene, styrene-butadiene rubber, styrene-butadiene-styrene block copolymer, styrene-isoprene-styrene block copolymer, styrene-ethylene-butylene-styrene block copolymer, and the like) or with thermoplastic synthetic resins (for example, polystyrene, styrene-acrylonitrile copolymer, acrylonitrile-butadiene-styrene copolymer, polyamide, polyethylene terephthalate, polybutylene terephthalate, polyvinyl chloride, and so forth). Propylene homopolymers, crystalline ethylene-propylene random copolymers and ethylene-propylene block copolymers that have propylene as the main ingredient, and crystalline propylene-based polymers, such as ethylene-propylene-butene-1 tertiary copolymers, propylene-hexene-butene-1 tertiary copolymers, and the like, are especially desirable.

Examples of compound A used in the present invention include: α , β , γ , ζ , ε , η , and δ tocopherols and mixtures thereof; 2,5-dimethyl substitutes, 2,5,8-trimethyl substitutes, and 2,5,7,8-tetramethyl

substitutes of 2-(4-methyl-penta-3-enyl)-6-hydroxychroman; 2,2,7-trimethyl-5-t-butyl-6-hydroxychroman; 2,2,5-trimethyl-7-t-butyl-6-hydroxychroman; 2,2,5-trimethyl-6-t-butyl-6-hydroxychroman; 2,2-dimethyl-5-t-butyl-6-hydroxychroman; and the like. Especially desirable are the aforesaid various kinds of tocopherols and mixtures of these. An example of compound B is 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene. Examples of compound C include tetrakis(2-t-butylphenyl)-4,4'-biphenylene-di-phosphonite, tetrakis(2-t-butyl-4-methylphenyl)-4,4'biphenylene-di-phosphonite, tetrakis(2,4-di-t-butylphenyl)-4,4'-biphenylene-di-phosphonite, tetrakis(2,4-di-nonylphenyl)-4,4'-biphenylene-di-phosphonite, and so forth, of which tetrakis(2,4-di-t-butylphenyl)-4,4'-biphenylene-di-phosphonite is especially preferable. The compounding proportions of compound A and compound B or compound C are respectively from 0.01 to 1 part by weight, preferably from 0.01 to 0.5 part by weight, per 100 parts by weight of a polyolefin. If the compounded quantities of these components are less than 0.01 part by weight, the resulting composition does not exhibit the desired thermal process stability to a satisfactory degree. Although quantities exceeding 1 part by weight pose no problem, no further improvement of the thermal process stability can be expected; therefore, this range is not only impractical but also not cost efficient.

In the composition of the present invention, various kinds of additives that are commonly added to polyolefins may be used

concomitantly within the extent that does not adversely affect the objectives of the present invention, examples of said additives including: phenol-based, thioether-based, and phosphorus-based antioxidants; light stabilizers; clarifying agents; nucleating agents; lubricating agents; antistatic agents; anticorrosion agents; antiblocking agents; droplet-proof agents; colorants; heavy metal deactivators (copper inhibitors); radical generating agents, such as peroxides and the like; dispersion agents or neutralizing agents, such as metal salts and the like; inorganic fillers (for example, talc, mica, clay, wollastonite, zeolite, asbestos, calcium carbonate, aluminum hydroxide, magnesium hydroxide, barium sulfate, calcium silicate, glass fibers, carbon fibers, and the like); the aforesaid inorganic fillers that are surface-treated with surface-treatment agents, such as coupling agents (for example, silane-based, titanate-based, boron-based, aluminate-based, and zircoaluminate-based agents); and organic fillers (for example, wood powder, pulp, recovered paper, synthetic fibers, natural fibers, and the like.)

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The composition of the present invention can be obtained by mixing a polyolefin with the predetermined quantities of the aforesaid compound A, compound B or compound C, and the aforesaid various kinds of additives that are commonly added to polyolefins with a conventional mixing apparatus, such as a Henschel mixer (a product name), super mixer, ribbon blender, Banbury mixer, or the like, and by melting, kneading, and pelletizing the mixture with an ordinary single

screw extruder, twin screw extruder, pravender [as transliterated], rollers, or the like at a melting/kneading temperature of from 150 °C to 300 °C, preferably from 180 °C to 250 °C. The obtained composition is used for the production of the intended molded products by various kinds of forming methods, including injection molding, extrusion molding, blow molding, and the like.

The composition of the present invention exhibits excellent process stability in the molding stage, and it also has the excellent effect of preventing coloration caused by the antioxidant used therein, thus rendering itself useful for various molded products, particularly useful for applications that require safety for the human body, including food packages, food containers, medical containers, toys, and the like.

[Operation]

With respect to how the concomitant use of compound A with compound B or C works in the present invention in the process of melting and kneading the polyolefin composition, the working mechanism proper has not been elucidated yet. However, it is commonly known that the phenolic antioxidants that are referred to as compound B work as a radical chain inhibitor and that the phosphonite compounds that are referred to as compound C act as a peroxide decomposer. The concomitant use of the aforesaid compound A with compound B or compound C was found to have remarkable synergistic effects that could

not be expected from the heretofore-known combination with 6-hydroxychroman compounds.

[Effects]

The composition of the present invention exhibits far superior thermal process stability in a molding process and coloring inhibiting property to those of nontoxic polyolefin compositions in which are compounded 6-hydroxychroman compounds according to the heretofore-known combination.

[Working Examples]

The following will explain the present invention in detail by presenting working examples and comparative examples, but the present invention will not be limited to or restricted by these examples.

The evaluation methods used in the working examples and comparative examples are as follows.

I) Thermal process stability

(a) When the polyolefin used was a propylene polymer:

The melt flow rate (MFR) of the obtained pellets was measured (in accordance with JIS K6758) and referred to as the first MFR. Then, the obtained pellets were melted/kneaded repeatedly at a melting/kneading temperature of 270 °C, and the MFR of the pellets thus obtained was measured and referred to as the second MFR.

Thermal process stability was evaluated based on the magnitude of the numeric value of this second MFR and the numeric value of ΔMFR:

$$\Delta MFR = \text{the second MFR} - \text{the first MFR.}$$

The smaller these numeric values are, the better process stability the composition has in repeated extrusion, in other words, in a molding process.

(b) When the polyolefin used was an ethylenic polymer:

The melt index (MI) of the obtained pellets was measured (in accordance with JIS K6760) and referred to as the first MI. Then, the obtained pellets were melted and kneaded repeatedly at a melting/kneading temperature of 270 °C, and the MI of the pellets thus obtained was measured and referred to as the second MI.

Thermal process stability was evaluated based on the magnitude of the numeric value of this second MI and the numeric value of ΔMI :

$\Delta MI = \text{the first MI} - \text{the second MI}$.

The smaller these numeric values are, the better process stability the 1/6 composition has in repeated extrusion, in other words, in a molding process.

II) Coloring inhibiting property: The YI (yellowness index) of the obtained pellets was measured (in accordance with JIS K7103), and the YI value found here was referred to as the first YI. Then, the obtained pellets were melted and kneaded repeatedly at a melting/kneading temperature of 270 °C, and the YI of the pellets thus obtained was measured and referred to as the second YI.

The coloring inhibiting property was evaluated based on the magnitude of the numeric value of this second YI and the numeric value of ΔYI :

ΔYI = the second YI - the first YI.

The smaller these numeric values are, the better coloring inhibiting property the composition has.

Working Examples 1 and 2 and Comparative Examples 1 through 8

Per 100 parts by weight of a powdered propylene homopolymer having an MFR (the discharge rate of a melted resin per 10 minutes under the application of a 2.16 kg load at 230 °C) of 2.0 g/10 minutes as the polyolefin, dl- α -tocopherol as compound A, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-hydroxybenzyl)benzene as compound B, tetrakis(2,4-d-t-butylphenyl)-4,4'-biphenylene-di-phosphonite as compound C, and other additives in the quantities specified in Table 1 below were placed in a Henschel mixer (a product name) and stirred and mixed for 3 minutes, after which the mixture was melted, kneaded, and pelletized at 200 °C with a single screw extruder having a bore size of 40 mm. As Comparative Examples 1 through 8, to 100 parts by weight of a powdered propylene homopolymer having an MFR of 2.0 g/10 minutes, the additives shown in Table 1 below were compounded in the prescribed quantities, and, in the same manner as in Working Examples 1 and 2, they were stirred/mixed and melted/kneaded, thereby obtaining pellets.

The obtained pellets were tested for thermal process stability and coloring inhibiting property by the test methods described in the foregoing.

The obtained results are shown in Table 1.

Working Examples 3 and 4 and Comparative Examples 9 through 16

Per 100 parts by weight of a powdered ethylene-propylene random copolymer (ethylene content: 2.5 % by weight) having an MFR (the discharge rate of a melted resin per 10 minutes under the application of a 2.16 kg load at 230 °C) of 7.0 g/10 minutes as the polyolefin, dl- α -tocopherol as compound A, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-hydroxybenzyl)benzene as compound B, tetrakis(2,4-d-t-butylphenyl)-4,4'-biphenylene-di-phosphonite as compound C, and other additives in the quantities specified in Table 2 below were placed in a Henschel mixer (a product name) and stirred and mixed for 3 minutes, after which the mixture was melted, kneaded, and pelletized at 200 °C with a single screw extruder having a bore size of 40 mm. As Comparative Examples 9 through 16, to 100 parts by weight of a powdered ethylene-propylene random copolymer (ethylene content: 2.5 % by weight) having an MFR of 7.0 g/10 minutes, the additives shown in Table 2 below were compounded in the prescribed quantities, and, in the same manner as in Working Examples 3 and 4, they were stirred/mixed and melted/kneaded, thereby obtaining pellets.

The obtained pellets were tested for thermal process stability and coloring inhibiting property by the test methods described in the foregoing. The obtained results are shown in Table 2.

Working Examples 5 and 6 and Comparative Examples 17 through 24

Per 100 parts by weight of a powdered ethylene-propylene block copolymer (ethylene content: 8.5 % by weight) having an MFR (the discharge rate of a melted resin per 10 minutes under the application

of a 2.16 kg load at 230 °C) of 4.0 g/10 minutes as the polyolefin, dl- α -tocopherol as compound A, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-hydroxybenzyl)benzene as compound B, tetrakis(2,4-d-t-butylphenyl)-4,4'-biphenylene-di-phosphonite as compound C, and other additives in the quantities specified in Table 3 below were placed in a Henschel mixer (a product name) and stirred and mixed for 3 minutes, after which the mixture was melted, kneaded, and pelletized at 200 °C with a single screw extruder having a bore size of 40 mm. As Comparative Examples 17 through 24, to 100 parts by weight of a powdered ethylene-propylene block copolymer (ethylene content: 8.5 % by weight) having an MFR of 4.0 g/10 minutes, the additives shown in Table 3 below were compounded in the prescribed quantities, and, in the same manner as in Working Examples 5 and 6, they were stirred/mixed and melted/kneaded, thereby obtaining pellets. /7

The obtained pellets were tested for thermal process stability and coloring inhibiting property by the test methods described in the foregoing. The obtained results are shown in Table 3.

Working Examples 7 and 8 and Comparative Examples 25 through 32

Per 100 parts by weight of a powdered Ziegler-Natta type ethylene homopolymer having an MI (the discharge rate of a melted resin per 10 minutes under the application of a 2.16 kg load at 190 °C) of 5.0 g/10 minutes as the polyolefin, dl- α -tocopherol as compound A, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-hydroxybenzyl)benzene as compound B, tetrakis(2,4-d-t-butylphenyl)-4,4'-biphenylene-di-phosphonite as

compound C, and other additives in the quantities specified in Table 4 below were placed in a Henschel mixer (a product name) and stirred and mixed for 3 minutes, after which the mixture was melted, kneaded, and pelletized at 200 °C with a single screw extruder having a bore size of 40 mm. As Comparative Examples 25 through 32, to 100 parts by weight of a powdered Ziegler-Natta type ethylene homopolymer having an MI of 5.0 g/10 minutes, the additives shown in Table 4 below were compounded in the prescribed quantities, and, in the same manner as in Working Examples 7 and 8, they were stirred/mixed and melted/kneaded, thereby obtaining pellets.

The obtained pellets were tested for thermal process stability and coloring inhibiting property by the test methods described in the foregoing. The obtained results are shown in Table 4.

The compounds and additives pertaining to the present invention that are shown in Tables 1 through 4 are as follows.

Compound A: dl- α -tocopherol

Compound B: 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene

Compound C: tetrakis(2,4-di-t-butylphenyl)-4,4'-biphenylene-di-phosphonite

Phenolic antioxidant 1: 2,6-di-t-butyl-p-cresol

Phenolic antioxidant 2: tris(3,5-di-t-butyl-4-hydroxybenzyl)isocyanurate

Phenolic antioxidant 3: tetrakis[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate]methane

Thioether antioxidant: dimyristyl thiodipropionate

Phosphorus-based antioxidant 1: tris(nonylphenyl)diphosphite

Phosphorus-based antioxidant 2: distearyl pentaerythritol diphosphite

Ca-St: calcium stearate

TABLE 1

	(a) JUNEN		(b) M		C		R			
	1	2	1	2	3	4	5	6	7	8
G	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
G	0.02	—	—	—	—	—	—	—	—	—
G	0.03	—	—	—	—	—	—	—	—	—
フ	—	—	—	—	—	—	—	—	—	—
フ	—	—	—	—	—	—	—	—	—	—
フ	—	—	—	—	—	—	—	—	—	—
フ	—	—	—	—	—	—	—	—	—	—
フ	—	—	—	—	—	—	—	—	—	—
フ	—	—	—	—	—	—	—	—	—	—
リ	—	—	—	—	—	—	—	—	—	—
リ	—	—	—	—	—	—	—	—	—	—
リ	—	—	—	—	—	—	—	—	—	—
CA-ST	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
M 1 M F R (G)	1.1	1.1	2.5	2.1	1.7	1.9	1.0	2.1	1.0	1.8
M 2 M F R (H)	0.7	2.8	4.9	5.5	3.9	3.1	3.0	4.7	1.0	2.3
M M F R	1.0	1.2	2.4	1.9	1.3	1.5	1.8	2.1	2.0	1.5
M (Y) (I)	2.5	2.0	4.8	6.6	4.2	4.6	4.4	6.0	2.0	2.8
M 2 Y (J)	4.0	4.9	14.5	22.5	12.4	11.1	16.3	6.5	5.5	6.1
A Y I	2.1	2.6	19.2	15.7	8.3	6.7	1.9	4.5	3.1	4.3

Key: a) working example; b) comparative example; c) composition (* parts by weight); d) phenolic antioxidant; e) thioether antioxidant; f) phosphorus-based antioxidant; g) first MFR; h) second MFR; i) first YI; j) second YI; A, B, C) compound

(Note) * parts by weight of additives per 100 parts by weight of a resin.

ΔMFR = the second MFR - the first MFR

ΔYI = the second YI - the first YI

TABLE 2

	(A) 酸素	(B) 水								酸	碱
		0	4	9	18	31	42	53	64		
化 合 物 A	0.02	0.03	0.05	0.05	0.03	0.03	0.02	0.03	0.05	0.03	—
化 合 物 B	0.02	—	—	—	—	—	—	—	—	—	—
化 合 物 C	—	0.02	—	—	—	—	—	—	—	—	—
フタル酸二水素鉄(Ⅱ)(a)	—	—	—	—	—	0.03	—	—	—	—	—
フタル酸二水素鉄(Ⅲ)(a)	—	—	—	—	—	—	0.05	—	—	—	—
フタル酸二水素鉄(Ⅳ)(a)	—	—	—	—	—	—	—	0.05	—	—	—
チオカルバミル酸二水素鉄(Ⅱ)(a)	—	—	—	—	—	—	—	—	0.03	—	—
ソルビカルバミル酸二水素鉄(Ⅱ)(a)	—	—	—	—	—	—	—	—	—	0.03	—
ソルビカルバミル酸(Ⅴ)(a)	—	—	—	—	—	—	—	—	—	—	0.03
Ca-SI	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ca-MFR (g)	8.5	6.0	7.8	3.0	8.8	8.9	7.3	7.5	7.6	6.7	—
Ca-MFR (n)	8.8	6.1	4.4	12.0	9.7	1.1	1.1	1.7	18.0	19.5	8.3
Ca-MFR (p)	2.3	2.5	6.2	1.7	2.0	3.5	8.8	8.0	8.0	8.0	—
Ca-YI (1)	2.7	2.5	4.5	6.6	4.4	4.0	4.5	4.3	2.4	6.6	—
Ca-YI (2)	1.0	5.2	4.7	21.6	15.4	11.7	10.6	10.6	10.6	10.6	—
Ca-YI (3)	2.0	2.7	16.2	16.0	8.5	8.5	8.1	8.1	8.0	8.5	—

Key: a) working example; b) comparative example; c) composition (* parts by weight); d) phenolic antioxidant; e) thioether antioxidant; f) phosphorus-based antioxidant; g) first MFR; h) second MFR; i) first YI; j) second YI; A, B, C) compound

(Note) * parts by weight of additives per 100 parts by weight of a resin.

AMFR = the second MFR - the first MFR

ΔYT = the second YT - the first YT

TABLE 3

	(a)実験例			(b)比較			#		#	
	6	12	17	18	19	20	21	22	23	24
化合物A	0.40	0.15	0.23	0.05	5.02	0.03	0.32	0.05	0.03	0.05
化合物B	0.80	—	—	—	—	—	—	—	—	—
化合物C	—	0.05	—	—	—	—	—	—	—	—
フェノール系酸化防止剤 (d)	—	—	—	—	0.93	—	—	—	—	—
フェノール系酸化防止剤 (d)	—	—	—	—	—	0.69	—	—	—	—
フェノール系酸化防止剤 (d)	—	—	—	—	—	—	0.61	—	—	—
チオエーテル系酸化防止剤 (e)	—	—	—	—	—	—	3.45	—	—	—
リン酸化物 (f)	—	—	—	—	—	—	—	—	0.02	—
リン酸化物 (f)	—	—	—	—	—	—	—	—	—	0.03
Ca-Si	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
M 1 M F R (g)	2.9	2.4	4.5	4.5	2.9	2.8	4.1	4.4	4.6	3.8
M 2 M F R (h)	1.7	4.9	5.1	8.1	0.5	4.8	9.0	9.7	8.0	5.6
M F R	1.4	1.5	4.6	3.2	2.0	2.9	3.1	4.2	4.1	4.6
M 1 Y I (i)	2.6	2.6	4.2	5.7	1.0	4.8	4.1	4.2	5.6	4.5
M 2 Y I (j)	5.0	3.2	15.0	22.5	12.0	11.0	11.2	8.7	16.7	9.2
ΔY I	2.4	2.6	16.7	16.8	4.6	7.2	6.6	4.8	14.2	5.3

Key: a) working example; b) comparative example; c) composition (* parts by weight); d) phenolic antioxidant; e) thioether antioxidant; f) phosphorus-based antioxidant; g) first MFR; h) second MFR; i) first YI; j) second YI; A, B, C) compound

(Note) * parts by weight of additives per 100 parts by weight of a resin.

$\Delta\text{MFR} = \text{the second MFR} - \text{the first MFR}$

$\Delta\text{YI} = \text{the second YI} - \text{the first YI}$

TABLE 4

	(a) WORKING EXAMPLE			(b) COMPARATIVE EXAMPLE			MI			PI		
	7	8	22	26	27	28	26	30	31	32	33	
化合物 A	5.03	5.03	5.03	6.05	6.05	6.05	5.03	5.03	5.03	5.03	5.03	5.03
化合物 B	5.01	—	—	—	—	—	—	—	—	—	—	—
化合物 C	—	5.03	—	—	—	—	—	—	—	—	—	—
フタノール系酸化防止剤 1 (d)	—	—	—	—	5.03	—	—	—	—	—	—	—
フタノール系酸化防止剤 2 (d)	—	—	—	—	—	5.03	—	—	—	—	—	—
フタノール系酸化防止剤 3 (d)	—	—	—	—	—	—	5.03	—	—	—	—	—
チオエーテル系酸化防止剤 4 (e)	—	—	—	—	—	—	—	5.03	—	—	—	—
リソホスホ酸化防止剤 1 (f)	—	—	—	—	—	—	—	—	5.03	—	—	—
リソホスホ酸化防止剤 2 (f)	—	—	—	—	—	—	—	—	—	5.03	—	—
C ₆ H ₅ CO ₂ H	5.01	5.01	5.01	5.01	5.01	5.01	5.01	5.01	5.01	5.01	5.01	5.01
MI-1 MI-1 (g)	5.0	5.0	4.8	5.5	5.2	5.2	4.8	4.7	4.7	4.7	4.7	4.7
MI-2 MI-1 (h)	5.1	4.9	5.0	5.0	5.1	5.0	5.4	3.6	2.5	5.1	—	—
d MI-1	5.0	9.4	1.0	1.5	1.1	1.2	1.0	1.7	1.7	1.7	1.7	1.7
MI-1 YI-1 (i)	2.8	2.7	4.6	0.7	4.3	3.1	4.5	4.6	2.8	4.3	—	—
MI-2 YI-1 (j)	6.4	8.6	14.5	22.7	23.1	21.1	12.3	8.8	11.1	2.4	—	—
d YI-1	2.6	2.6	11.0	17.4	8.8	7.2	5.6	4.6	8.4	2.4	—	—

Key: a) working example; b) comparative example; c) composition (* parts by weight); d) phenolic antioxidant; e) thioether antioxidant; f) phosphorus-based antioxidant; g) first MI; h) second MI; i) first YI; j) second YI; A, B, C) compound

(Note) * parts by weight of additives per 100 parts by weight of a resin.

ΔMI = the first MI - the second MI

ΔYI = the second YI - the first YI

In the working examples and comparative examples shown in Table 1, a propylene homopolymer was used as the polyolefin. As seen from Table 1, compound A and compound B or compound C pertaining to the present invention were used in Working Examples 1 and 2, and the comparison between Working Examples 1 and 2 and Comparative Examples 1 and 2 (compositions with compound A alone) shows us that Working Examples 1 and 2 have superior thermal process stability and coloring inhibiting properties. When Working Examples 1 and 2 are compared with

Comparative Examples 3 through 5, which were compositions in which compound A and heretofore-known phenolic antioxidants were concomitantly used, it can be seen that Comparative Examples 3 through 5 had considerably improved thermal process stability, but not to a satisfactory degree, and the coloring inhibiting effect was also not satisfactory. Similarly, the comparison of Comparative Example 6, in which a thioether antioxidant (thiodipropionic acid ester) was concomitantly used, to Working Examples 1 and 2 shows us that the coloring inhibiting property was improved substantially, but not to a satisfactory degree, and the improvement effect on thermal process stability was also not satisfactory. When Comparative Examples 7 and 8, in which were used phosphorus-based antioxidants other than compound C pertaining to the present invention, are compared with Working Examples 1 and 2, it can be seen that Comparative Examples 7 and 8 were inferior in every aspect and that the compositions of the present invention exhibited remarkable synergistic effects. /9

When the synergistic effects of compound B and of compound C with compound A in Working Examples 1 and 2 pertaining to the present invention are compared, it can be seen that compound B, which is a phenolic antioxidant, is superior to compound C, which is a phosphorus-based antioxidant. This can be said to be a unique effect that was found in the present invention, that is, in the concomitant use with compound A, considering the fact that a phosphorus-based

antioxidant exhibits an excellent synergistic effect with a common phenolic antioxidant.

Tables 2 through 4 show the compositions in which, as the polyolefin, an ethylene-propylene random copolymer, ethylene-propylene block copolymer, and Ziegler-Natta type ethylene homopolymer were respectively used, and they also were found to have the same effects as those described in the foregoing.

From the above, it can be seen that the compositions of the present invention are superior in every aspect to heretofore-known compositions in which compound A alone is used or in which it is used concomitantly with various kinds of compounds, thus confirming the remarkable effects of the compositions of the present invention.